Low Viscosity Dispersion for Paper or Textile Processing

Background of the Invention

This invention relates to concentrated, low-viscosity aqueous dispersions for the treatment of paper and textiles, to a process for the production of these dispersions and to the use of the dispersions for the softening of paper and textiles.

For many paper and textile products, softness is an important requirement. Thus, consumers expect textiles or paper products, for example paper handkerchiefs, household towels or sanitary articles, to feel soft. Accordingly, numerous suitable compounds and compositions are known for the softening of paper and textiles. It is known from **US 3,594,224** that certain quaternary ammonium compounds are suitable for improving the softness of cellulose fibers. **WO 96/08601** proposes a polysiloxane-containing composition for treating tissue products which, besides polysiloxanes, also contains a polyhydroxy compound, such as polyethylene glycol or glycerol. **WO 94/10381** describes mixtures of quaternary ammonium compounds and polyethylene glycol or polypropylene glycol for the softening of paper products and cellulose-containing fibers. **EP 569 847 A1** describes alkoxylated natural oils and fats as active ingredients of fabric softener formulations. **EP 494 769 A2** describes fabric softeners based on pentaerythritol esters. **EP 698 140 B1** claims tissue paper treated with a three-component softener. Sorbitan fatty acid esters are used as the softening component. These compounds are formulated as aqueous dispersions and are suitably applied to the products. EP 698 140 B1 proposes nonionic emulsifiers, such as alkyl (oligo)glycosides or ethoxylated or propoxylated sorbitan esters in combination with selected polyhydroxy compounds, as a suitable emulsifier system.

However, the compositions mentioned above often contain only up to 10% by weight of active substances because dispersions with higher

concentrations can also have a greatly increased viscosity which makes direct processing, for example by spraying onto textile or paper webs, difficult or even impossible. Highly concentrated dispersions also tend to separate or break up more quickly and show reduced stability in storage.

Accordingly, the problem addressed by the present invention was to provide concentrated, but low-viscosity compositions in the form of aqueous dispersions for the softening of paper and textiles.

It has been found that dispersions containing a selected softener combination based on glycerol and derivatives thereof satisfy the low-viscosity and high-stability requirements mentioned above.

Brief Summary of the Invention

Accordingly, the present invention relates to concentrated, low-viscosity aqueous dispersions for the softening of paper and textiles which contain

a) a nonionic softener component selected from monoesters or diesters of glycerol with C_{8-22} fatty acids and mixtures thereof,
b) a polyol compound,
c) cationic and nonionic emulsifiers,
d) 70 to 90% by weight water

and optionally other auxiliaries and additives, the ratio by weight of component a) to component b) being from 2.5:1 to 1:2.5.

Detailed Description of the Invention

The dispersions according to the invention are low-viscosity dispersions, i.e. they preferably have a Brookfield viscosity in the range from 1 to 100 mPa·s and more particularly in the range from 1 to 50 mPa·s, as measured at 20°C (spindle 1, 20 r.p.m.). Dispersions with a viscosity below 10 mPa·s are particularly preferred. The water content is between 70 and 90% by weight, dispersions containing less than 80% by weight water being preferred. The dispersions are fine-particle storage-stable dispersions and may be directly applied to the paper or to the textiles. There is no need for additional dilution or other conditioning.

The dispersions are generally suitable for the softening of paper or

textiles. They may be used both for permanent softening and also for temporary softening. Thus, the dispersions may be used during the production or finishing of paper products or textiles or as an aftertreatment or fabric softener in washing machines or institutional laundries or as a tumbler aid.

In the context of the present invention, textiles are understood to be any textile piece goods which contain synthetic or natural fibers, for example wool, cotton, polyamide, polyester or polyacrylic fibers or blends of these fibers. However, the textile fibers themselves may be treated with the dispersions. Besides paper and paper products, cellulose-containing fibers, for example chemical and mechanical pulp fibers, and fleeces or nonwovens of these fibers may also be treated with the dispersions. The dispersions are preferably used for the softening of paper and paper products, including for example tissue paper which is used in the manufacture of handkerchiefs, kitchen or household towels, and sanitary articles, such as tampons, toilet paper and diapers.

In the treatment of paper or textiles, any processes known to the expert for applying liquid treatment compositions may be used, including for example print coating, spray coating, slop-padding, padding, size press coating, air-jet coating, air-knife coating, roll coating or gravure coating. To this end, textile or paper webs are generally contacted with the dispersions in suitable machines in which the dispersions are applied to the textile or to the paper in suitable quantities. Textiles may also be treated by absorption processes in which the textile remains in the aqueous dispersion and the active substances are absorbed onto the fibers. The dispersions may even be used in heated form, i.e. at temperatures of up to 80°C.

So far as the finishing of paper/paper products is concerned, processes of the type in question are described, for example, in **Handbook of Paperboard and Board, R.R.A. Higham, BB Ltd, London 1970, pages 142 to 169** and, for textiles, in **Veredelung von Textilien, VEB**

Fachbuchverlag Leipzig 1990, pages 193 to 228.

The dispersions contain monoesters or diesters of glycerol with C_{8-22} fatty acids, which may be linear or branched, saturated or unsaturated, as the nonionic softening component a). Glycerol esters based on saturated linear fatty acids, for example lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid or behenic acid or mixtures thereof, are particularly suitable. The monoglycerides or diglycerides may also be used in the form of the mixtures accumulating in the industrial-scale production process. The glycerides may also be present in mixtures of mono- and diglycerides. However, dispersions containing at least 60% by weight of diglycerides, based on the softener component a), are preferred. The dispersions contain the nonionic softener component a) in quantities of preferably 1 to 14% by weight, dispersions containing the softener in quantities of 5 to 10% by weight being particularly preferred.

The dispersions contain at least one polyol compound b) as another key ingredient in such quantities that the ratio by weight of the nonionic softener component to the polyol compound is in the range from 2.5:1 to 1:2.5 and preferably in the range from 2.0:1 to 1:1. A polyol compound in the context of the present invention is understood to be an organic compound containing at least two carbon atoms and at least two hydroxyl groups in the molecule, the hydroxyl groups not being derivatized. Suitable polyol compounds are, for example, glycerol and dimers or trimers thereof, glycols and polymers thereof, pentaerythritol, di- and trimethylol propane, sorbitan, mannitol, xylitol, glucose, mannose or fructose.

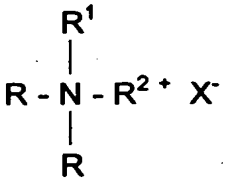
The dispersions preferably contain glycerol, diethylene glycol, polyethylene glycol or 1,2-propylene glycol and mixtures thereof as the polyol compound. Other preferred dispersions are those which contain polyethylene glycol with an average molecular weight in the range from 200 to 1000 and preferably in the range from 200 to 600.

The percentage content of polyol compounds b) is preferably in the

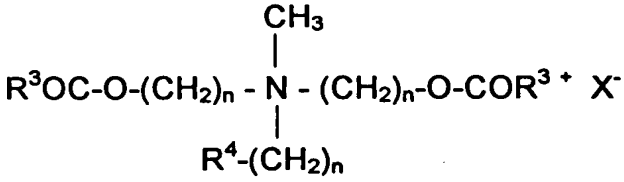
range from 1.0 to 12.0% by weight and more preferably in the range from 5 to 10% by weight. Mixtures of glycerol with polyethylene glycol are particularly suitable, mixtures in which the ratio by weight of glycerol to polyethylene glycol is from 10:1 to 6:1 being particularly preferred. The glycols are present in quantities of preferably 0.1 to 2.0% by weight and more preferably 0.1 to 1.0% by weight.

The dispersions according to the invention contain a system of cationic and nonionic emulsifiers as emulsifiers c) for the nonionic softeners. Particularly suitable nonionic emulsifiers are fatty acids and fatty alcohols or derivatives thereof, particularly reaction products thereof with alkylene oxides, such as ethylene oxide, propylene oxide and/or butylene oxide. Preferred cationic emulsifiers are compounds containing at least one cationically charged nitrogen atom.

Suitable cationic emulsifiers are preferably selected from the group of quaternary ammonium compounds corresponding to formulae (I) and (II):



(I)



(II)

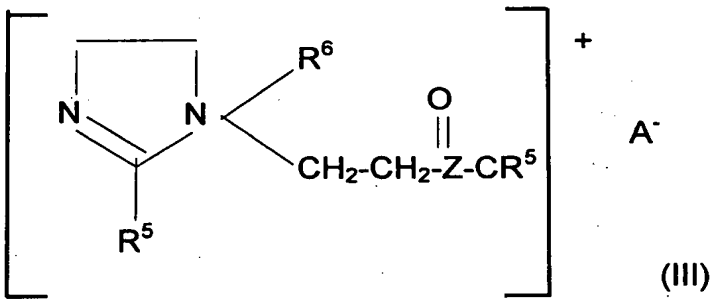
in which R is an acyclic alkyl group containing 12 to 24 carbon atoms, R^1 is a saturated C_{1-4} alkyl or hydroxyalkyl group, R^2 has the same meaning as R or R^1 and COR^3 stands for an aliphatic acyl group containing 12 to 22 carbon atoms and 0, 1, 2 or 3 double bonds and R^4 is hydrogen or OH, n has a value of 1, 2 or 3 and X is a halide, methosulfate, methophosphate or

C_{16-18} alkyl groups are particularly preferred.

Examples of cationic emulsifiers corresponding to formula (I) are didecyl dimethyl ammonium chloride, ditallow dimethyl ammonium chloride or dihexyldecyl dimethyl ammonium chloride. Examples of compounds corresponding to formula (II) are methyl-N,N-bis(acyloxyethyl)-N-(2-hydroxyethyl)-ammonium methosulfate, methyl-N-(2-hydroxyethyl)-N,N-di(tallowacyloxyethyl)ammonium methosulfate and bis-(palmitoyl)-ethylhydroxyethyl methyl ammonium methosulfate. Besides the compounds of formulae (I) and (II), short-chain water-soluble quaternary ammonium compounds, for example trihydroxyethyl methyl ammonium methosulfate or cetyl trimethyl ammonium chloride, may also be used. Protonated alkylamine compounds which have a softening effect are also suitable.

If quaternized compounds of formula (II) containing unsaturated alkyl chains are used, those acyl groups are preferred of which the corresponding fatty acids have an iodine value in the range from 5 to 25, preferably in the range from 10 to 25 and more preferably in the range from 15 to 20 and which have a cis/trans isomer ratio (in % by weight) of 30:70, preferably greater than 50;50 and more preferably greater than 70:30.

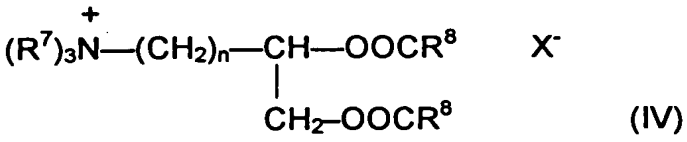
Besides the quaternary compounds described above, other known compounds, for example quaternary imidazolinium compounds corresponding to formula (III):



(III)

in which R^5 is a saturated alkyl group containing 12 to 18 carbon atoms, R^6 is an alkyl group containing 1 to 4 carbon atoms or hydrogen and Z is an NH group or oxygen and A is an anion,
may also be used.

Other suitable quaternary compounds correspond to formula (IV):



(IV)

in which the substituents R^7 selected independently of one another represent a C_{1-4} alkyl, alkenyl or hydroxyalkyl group, the substituents R^8 selected independently of one another represent a C_{8-28} alkyl group and n has a value of 0 to 5. X stands for an anion, for example a halide, methosulfate, methophosphate or phosphate ion. The dispersions according to the invention contain the cationic emulsifiers in quantities of preferably 0.5 to 3.0% by weight and more preferably 1.0 to 2.0% by weight.

In addition, the dispersions contain nonionic emulsifiers, preferably from the group of alkoxylated fatty acids containing 8 to 22 carbon atoms, alkoxylated fatty acid esters of fatty acids containing 8 to 22 carbon atoms with monohydric alcohols containing 1 to 10 carbon atoms and alkoxylated fatty alcohols containing 8 to 22 carbon atoms, the alkoxylated compounds having HLB values of 3 to 20 and preferably in the range from 8 to 16. The HLB (hydrophilic/lipophilic balance) value is a measure of the water or oil solubility of nonionic surfactants (cf. **Römpp Chemie Lexikon, Vol. 3, 9th Edition 1990, pages 1812-13**). It is defined by the following equation:

$$HLB = 20\left(1 - \frac{VZ}{SZ}\right)$$

where AV is the acid value and SV is the saponification value of the corresponding compound.

The fatty acid ester alkoxylates are known compounds which are described, for example, in **US 2,678,935, US 3,539,518, US 4,022,808** and **GB 1,050,497**, of which the disclosures also form part of the present application.

The alkoxylated fatty acid esters may be prepared by any of the methods known to the expert, for example by esterification of fatty acids with alkoxylated methanol, as described for example in **US 3,539,518**. Another method comprises directly reacting fatty acid esters with alkylene oxides in the presence of transition metal catalysts, as described in **US 4,022, 808**. However, the fatty acid alkyl ester alkoxylates are preferably produced by the heterogeneously catalyzed direct alkoxylation of fatty acid alkyl esters with ethylene oxide and/or propylene oxide on hydrophobicized hydrotalcites. These synthesis processes are described in detail in **WO 90/13533** and **WO 91/15441**, of which the disclosure is also part of the present application. The products formed are distinguished by a low OH value. The reaction is carried out in a single stage and gives light-colored products. The fatty acid alkyl esters used as starting materials may be obtained from natural oils or fats or may be synthetically produced.

Examples of particularly suitable nonionic emulsifiers are C_{12-18} fatty alcohols containing 7 to 14 moles of ethylene oxide per mole of alcohol and cetyl/stearyl alcohol containing 20 moles of ethylene oxide and C_{12-18} fatty acids or fatty acid esters with C_{1-4} alcohols which contain between 8 and 16 moles of ethylene oxide per mole of fatty acid or ester.

Other suitable nonionic emulsifiers are selected from the group of alkyl (oligo)glycosides corresponding to the formula R-O-$[Z]_x$, where R is an alkyl group containing 8 to 22 carbon atoms, Z is a sugar unit containing 5 or 6 carbon atoms and x is a number of 1 to 10. Alkyl (oligo)glycosides, their production and their use as surfactants are known, for example, from

DE 19 43 689 A1 and from **DE 38 27 543 A1**.

So far as the glycoside unit is concerned, both monoglycosides where a sugar unit is attached to the fatty alcohol by a glycoside linkage and oligomeric glycosides with a mean degree of oligomerization of up to about 2 are particularly suitable. In commercially available alkyl oligoglycosides, the glucoside unit is present as the glycoside.

The percentage content of nonionic emulsifiers is preferably between 0.1 and 3.0% by weight and more preferably between 0.5 and 1.5% by weight.

The dispersions contain water in quantities of 70 to 90% by weight as solvent d). Deionized water is preferably used, although tap water may also be used. The pH value of the dispersions is preferably in the range from 4.5 to 7.5 and more preferably in the range from 5.0 to 6.5 and may be adjusted by addition of suitable acids, for example HCl, or bases, such as aqueous sodium hydroxide solution.

Besides the described ingredients a) to d), the dispersions according to the invention may contain other auxiliaries and additives typically encountered in the treatment of paper and textiles, including for example biocides, preservatives, dyes, pearlizers, defoamers, soil-release compounds, UV filters, perfume oils and fragrances and other additives obtained from native sources, for example vitamins or plant extracts.

The described dispersions may be prepared by any methods known to the expert. However, the nonionic softener and the cationic emulsifier are preferably added together to a mixture of the other components (nonionic emulsifier, glycerol and water and optionally auxiliaries and additives). Depending on the melting points of the individual components, it may be necessary to heat the mixtures, generally to temperatures of 40 to 80°C. The crude dispersion is then intensively mixed.

The dispersions are fine-particle dispersions and contain at least 90% (number distribution) of particles smaller than 1000 nm and preferably

smaller than 500 nm in size. Accordingly, it is only possible to use homogenizers which are capable of transmitting sufficiently powerful shear forces in order to obtain the fine-particle dispersions required. Suitable homogenizers are, for example, high-pressure or ultrasonic homogenizers.

It has been found that the use of certain homogenizers leads to dispersions having particularly advantageous properties.

Accordingly, the present invention also relates to a process for the production of the dispersions described above, in which components a) to c) and the auxiliaries present, if any, are first dispersed in water and the crude dispersion obtained is subsequently homogenized under pressures of 10 to 600 bar in a high-pressure homogenizer known to the expert (for example of the type manufactured by APV Homogenisator GmbH, Lübeck). In this case, it is particularly preferred to carry out homogenization under pressures of 25 to 250 bar.

As is normally the case where high-pressure homogenizers are used, the crude dispersion is homogenized first under low pressures, i.e. in the range from 10 to 50 bar, and then under higher pressures above 50 bar. It can be of advantage to homogenize the dispersions several times under different pressures. In another preferred embodiment, the homogenization treatment is carried out at temperatures in the range from 20 to 100°C and preferably in the range from 25 to 70°C. Depending on the auxiliaries and additives used, therefore, it may even be preferred to add them to the dispersions after homogenization.

Examples

Three different dispersions were prepared by initially melting the nonionic softener with the cationic emulsifier at 70°C. The resulting melt was then added to the other components which had been introduced into a stirred tank reactor at 70°C, followed by stirring for 15 minutes. The crude dispersion thus obtained was cooled to room temperature and then

homogenized in a high-pressure homogenizer (manufacturer: APV Homogenisator GmbH, Lübeck, Model LAB 60/60) at 40°C once under a pressure of 50 car and twice under a pressure of 200 bar. The pH value of the dispersion was 5.5.

Only dispersion 1 according to the invention has the low viscosity required, comparison dispersions 2 and 3 having a high viscosity which was impossible to measure.

The composition of concentrates 1 to 3 is shown in Table 1:

Table 1 (quantities in % by weight active substance)

	1	2	3
Glycerol di-$C_{16/18}$-fatty acid ester	9.7	10.6	12
Glycerol	4.8	2.7	2.5
Polyethylene glycol MW 400	0.5	0.5	0.5
Dehyquart Au 46	1.4	1.5	1.4
Stantex S 6030	0.9	1.8	1.6
Ratio by weight of softener to glycerol	1.8:1	3.3:1	4.0;1
Viscosity [mPa·s]**	12.5	n.d.*	n.d.*

* not determined because the dispersion could not be homogenized at 40°C

** Brookfield, spindle 1, 20°C, 20 r.p.m. (RVF viscosimeter manufactured by Brookfield Eng. Ltd.)

Dehyquart Au 46 methyl-N,N-bis-(acyloxyethyl)-N-(2-hydroxyethyl)-ammonium methosulfate (Henkel)

Stantex S 6030 ethoxylated methyl laurate containing 12 parts of ethylene oxide (Henkel).